

Facile Syntheses of 4-Vinyl-1,2,3-triazole Monomers by Click Azide/Acetylene Coupling

KENICHI TAKIZAWA,^{1,2} HUNAID NULWALA,¹ RAYMOND J. THIBAUT,^{1,3} PETER LOWENHIELM,¹ KOHJI YOSHINAGA,⁴ KAREN L. WOOLEY,^{5,6} CRAIG J. HAWKER¹

¹Department of Chemistry and Biochemistry, Materials Research Laboratory, University of California, Santa Barbara, California 93106

²Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-Cho, Aoba-Ku, Yokohama 227-8502, Japan

³The Dow Chemical Company, B1608 Freeport, Texas 77598

⁴Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata, Kitakyushu, Fukuoka 804-8550, Japan

⁵Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130

⁶Department of Radiology, Washington University in St. Louis, St. Louis, Missouri 63110

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ABSTRACT: Synthetic strategies for the preparation of a new family of vinyl monomers, 4-vinyl-1,2,3-triazoles, have been developed. These monomers are noteworthy as they combine the stability and aromaticity of styrenics with the polarity of vinylpyridines and the structural versatility of acrylate/methacrylate derivatives. To enable the wide adoption of these unique monomers, new methodologies for their synthesis have been elaborated which rely on Cu-catalyzed azide/acetylene cycloaddition reactions—"click chemistry"—as the key step, with the vinyl substituent being formed by either elimination or Wittig-type reactions. In addition, one-pot "click" reactions have been developed from alkyl halides, which allow for monomer synthesis without isolation of the intermediate organic azides. The high yield and facile nature of these procedures has allowed a library of new monomers including the parent compound, 1-*H*-4-vinyl-1,2,3-triazole, to be prepared on large scales. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 2897–2912, 2008

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INTRODUCTION

The concept and utility of robust, efficient, and orthogonal (REO) chemistry is gaining significant attention in synthetic materials chemistry, because of the increasing importance of functionality and structural definition in all aspects of polymer research.¹ With the advent of "click"

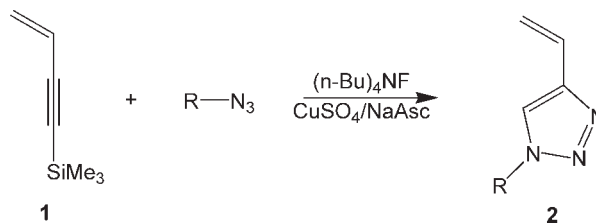
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Correspondence to: C. J. Hawker (E-mail: hawker@mrl.ucsb.edu)

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reactions, specifically the Cu(I)-catalyzed 1,3-dipolar cycloaddition of azides and alkynes,² the 1,2,3-triazole subunit has become a significant component of various small molecule and macromolecular systems, ranging from therapeutics, self-assembling systems, and responsive polymers³ to proton exchange membranes (PEM).⁴ This current interest is driven by the quantitative nature of the reaction, benign reaction conditions, and its compatibility with a wide range of functional groups. Significantly, little attention has been paid to the distinctive properties of the triazole nucleus with the vast majority of reports simply exploiting “click chemistry” and its associated triazole linkage as a connecting unit.⁵ This neglect/oversight is unfortunate, since it does not address the potentially more interesting aspect of combining the synthetic robustness and efficiency with the unique chemical and physical properties of the triazole ring itself.⁶

The ability to design functionalized macromolecules with new and/or improved physical properties is becoming fundamental to the development of new materials and click chemistry has the potential to significantly impact the range of functional polymers which are readily available.⁷ Unfortunately, the majority of polymer structures employed today is based on classical vinyl monomers, which limits the range of functional groups that can be used⁸ and the availability of new, highly functional monomer families has the potential to address many unmet needs. To alleviate this scarcity of new monomer families, 4-vinyl-1,2,3-triazoles have been designed to take advantage of the 1,2,3-triazole subunit and combine the features found in classical monomers, such as aromaticity, polarity, and structural diversity inherent in styrenics, vinylpyridines, and acrylates, respectively, into a single building block. By employing the highly efficient Cu(I)-catalyzed azide/acetylene coupling reaction, the syntheses of triazole-based monomers and their resulting macromolecules was reported recently and unique physical properties were observed for the polymers.⁹ The 4-vinyl-1,2,3-triazole monomers were synthesized via direct reaction of trimethylsilyl (TMS)-protected vinylacetylene with the corresponding organic azides using “click” chemistry conditions and, although high yields of the monomer units were obtained, this strategy suffered from a number of drawbacks. Most significantly, the preparation of TMS-protected vinylacetylene on a large scale



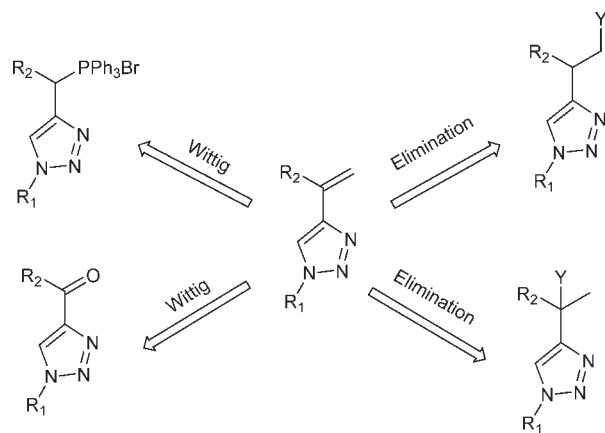
Scheme 1. Previous synthetic approach to vinyl triazole-based monomers, **2**.

is both synthetically difficult and prohibitively expensive and, therefore, necessitates the development of more scalable, lower cost procedures. In addressing this challenge, we report two alternative strategies based on elimination reactions and Wittig chemistry that offer efficient, high yielding and scalable synthetic pathways for the preparation of 4-vinyl-1,2,3-triazoles, thus enabling their widespread adoption.

RESULTS AND DISCUSSION

Previously, we reported the synthesis of 4-vinyl-1,2,3-triazole derivatives, **2**, by the *in situ* generation of 2-vinyl acetylene from 1-trimethylsilyl-2-vinyl acetylene, **1**,⁹ and coupling with the required azide (Scheme 1). While successful, this synthetic strategy suffered from a number of drawbacks, primarily the difficulty in the synthesis and handling of **1** and the associated high cost of the starting materials for the preparation of **1**. Routes for the synthesis of 4-vinyl-1,2,3-triazole have been reported by other groups, but these procedures include harsh reaction conditions with strong base or acid and low reported yields.^{3,10} To overcome these drawbacks and enable widespread availability of vinyl triazole-based monomers, new synthetic strategies for their synthesis are required.

In examining approaches for the preparation of vinyl triazole monomers, the high efficiency of azide/acetylene click chemistry, coupled with its compatibility toward a wide variety of functional groups, allows the coupling reaction to be performed early in the synthetic strategy and not as the last step, as described earlier. Incorporation of the triazole unit early in the synthetic route allows a much greater variety of starting materials to be used with retrosynthetic analyses leading to two dominant pathways (among others) for the synthesis of triazole based mono-



Scheme 2. Retrosynthetic analyses for the preparation of 4-vinyl-1,2,3-triazoles ($R_2 = \text{H}$ or Me) via Wittig- or elimination-based chemistries.

mers: a Wittig coupling strategy and an elimination pathway (Scheme 2).

Elimination Strategy

In selecting starting acetylene derivatives for the elimination strategy, the low cost and commercial availability of both 3-butyn-1-ol and 3-butyn-2-ol prompted an examination of their applicability for both the $3\pi + 2\pi$ cycloaddition as well as subsequent elimination reaction to give the desired vinyl triazole monomers. Initial work showed that traditional Cu(I)-catalyzed “click” coupling resulted in high yields and regioselectivity for formation of the triazole ring in both cases. Initial dehydration of the alcohol derivatives using SOCl_2 under reflux conditions, followed by reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was, however, not successful, with degradation being observed. (Scheme 3). It was found subsequently that mesylation of the “click” reaction product, 2-(1',2',3'-triazol-4'-yl)ethanol, using methanesulfonyl chloride (MsCl) followed by elimination using NaI and DBU gave substituted 4-vinyl-1,2,3-triazoles in excellent yield for a wide variety of substrates.¹¹ Alternatively, a one-pot elimination procedure using MsCl, Et_3N and NaI was also found to give the desired alkene in good yield. Examination of other elimination conditions, such as potassium *t*-butoxide (*t*-BuOK),¹² also gave excellent yields with unfunctionalized hydrocarbon substituents but reduced efficiency was observed with other functional groups.

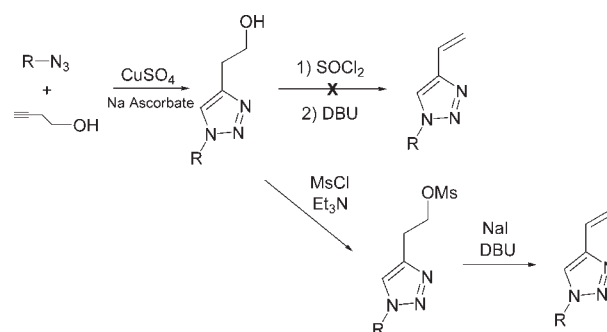
The potential hazard of handling organic azides, especially low molecular weight azides,

which are known to be explosive¹³ and difficult to handle because of their low boiling points and high N to C ratios, prompted the development of an alternative procedure for these materials. To circumvent the synthesis and/or use of azido derivatives, a “one-pot” synthesis, which requires no isolation of the organic azide, was examined and found to give yields comparable with those obtained when the preformed azides were employed.

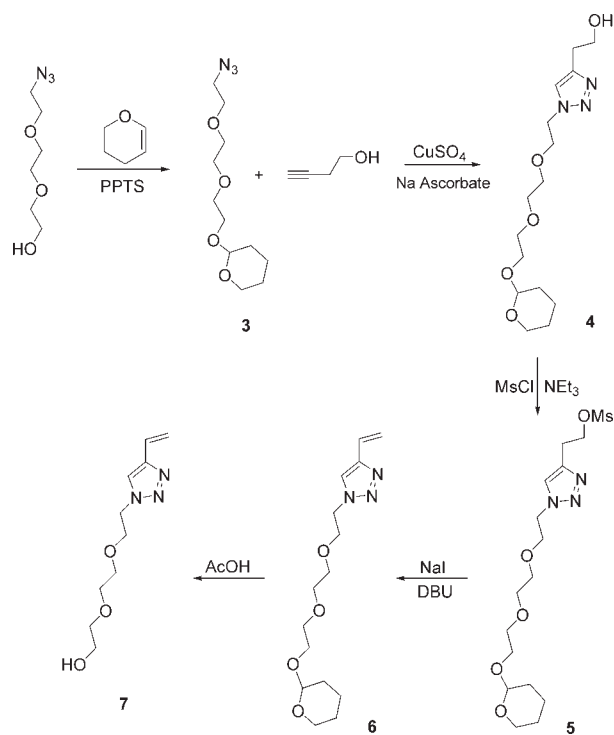
Although the elimination procedure is compatible with a range of functional groups, in the case of alcohol, thiol, or amino substituents, unwanted mesylation was found to occur at these functionalities. To overcome this lack of chemoselectivity, protection/deprotection strategies can easily be developed, as illustrated for the synthesis of the tri(ethylene glycol) derivative, **7**. This approach involves the use of a tetrahydropyran protecting group, which was shown to be compatible with the click coupling chemistry and subsequent elimination (Scheme 4).

Alternatively, the starting hydroxyl-functionalized alkyne could be initially mesylated, overcoming the necessity for the protection–deprotection steps described earlier and allowing mesylation to be performed prior to the cycloaddition reaction. As a result, mesylated alkynes such as **8** could be used directly for the synthesis of the vinyl triazole monomers, again demonstrating the compatibility of click chemistry with reactive functional groups (Scheme 5).

In analogy with the work described earlier with 3-butyn-1-ol as starting material, it was also shown that the isomeric 3-butyn-2-ol, **16**, could be used as an acetylene source. An advantage of **16** is that the secondary alcohol undergoes a more facile dehydration reaction when compared with the primary alcohol and, therefore, alleviates the necessity to form the



Scheme 3. Synthetic route for 4-vinyl-1,2,3-triazoles using elimination chemistry starting from but-3-yn-1-ol.

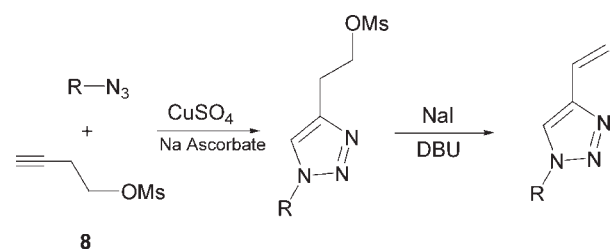


Scheme 4. Synthesis of the tri(ethylene glycol) derivative, **7**, using a protection/deprotection strategy.

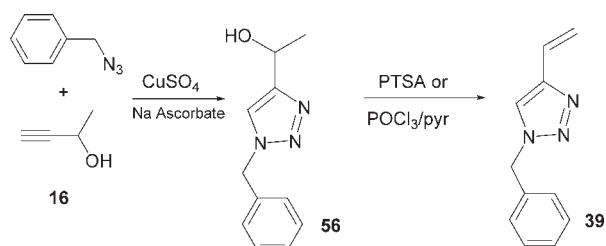
intermediate mesylate derivative. This advantage was shown to be the case with the intermediate secondary alcohol, **56**, which underwent facile dehydration directly to the alkene, **39**, in the presence of PTSA or POCl_3 /pyridine in 80–90% yield (Scheme 6).¹⁴

Wittig-Based Strategy

Having demonstrated the effectiveness of the elimination strategy for the preparation of a variety of functionalized 4-vinyl-1,2,3-triazole monomers, an alternative approach based on Wittig chemistry was examined. The low cost and wide availability of propargyl alcohol suggested a synthetic strategy involving an initial



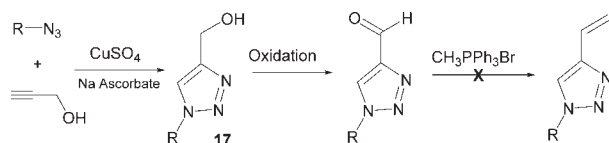
Scheme 5. Synthetic route for 4-vinyl-1,2,3-triazoles from mesylated starting materials, such as **8**.



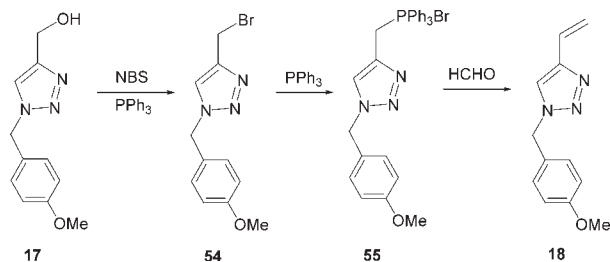
Scheme 6. Synthetic route for 4-vinyl-1,2,3-triazoles starting from 3-butyn-2-ol, **16**.

coupling of the desired azide or azide equivalent with propargyl alcohol to give the hydroxy-methyl substituted triazole, **17**. Oxidation with MnO_2 following literature procedures^{10(c)} proved to afford only low yields of the aldehyde; however, the use of Swern or Dess-Martin conditions was found to be more efficient giving the desired aldehyde in 80–90% yield. Unfortunately, all attempts to form the vinyl-substituted triazole by reaction with methyltriphenylphosphonium bromide gave only very low yields (<10%) and utilization of CH_2Br_2 -Zn-TiCl₄, which is known as a better reagent for adding one carbon atom to give a vinyl group¹⁵ did not afford any product (Scheme 7).

As shown earlier, one of the advantages of the Cu-catalyzed azide-alkyne coupling chemistry is its high tolerance of functional groups, which allows the reaction sequence or starting material structure to be easily modified. This versatility allows the original Wittig-based synthetic strategy to be reversed and a triazole-derived phosphine-ylide to be employed. Initial synthesis of the bromomethyl-substituted triazole, **54**, by reaction of propargyl bromide with a variety of azide derivatives did not afford high yields of **54** (<50%) and, as a result, a two-step procedure involving bromination of the hydroxymethyl derivative, **17**, was explored. Reaction of **17** with *N*-bromosuccinimide and triphenylphosphine afforded **54**, from which the ylide, **55**, could be obtained and Wittig coupling with formaldehyde was found to give the desired vinyl derivative, **18**, in greater than 80% yield over both steps (Scheme 8).



Scheme 7. Attempted synthesis of 4-vinyl-1,2,3-triazoles starting from propargyl alcohol.



Scheme 8. Synthetic route for 4-vinyl-1,2,3-triazoles using Wittig chemistry involving final coupling with formaldehyde.

Synthesis of 1-*H*-4-vinyl-1,2,3-triazole, **19**

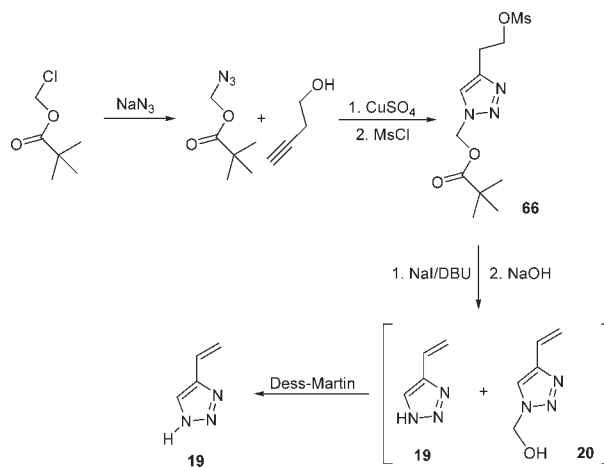
While the traditional synthesis of 1-unsubstituted triazole derivatives is complicated by the potentially dangerous and expensive use of HN_3 , the success demonstrated earlier in the synthesis of regiospecific 1-substituted 4-vinyl-1,2,3-triazole prompted the exploration of a protection/deprotection strategy for the preparation of the parent 1-*H*-4-vinyl-1,2,3-triazole, **19**. An additional motivation for this study is the recent report that 1-*H*-triazole-based materials show significant promise for applications ranging from catalytic supports to proton exchange membranes, with the highly polar and basic nature of the unsubstituted triazole ring being a major contributing factor to the improved performance of these materials.⁴

Initially, benzyl (Bn) and *p*-methoxybenzyl substituted triazole derivatives were prepared and hydrogenolysis of the benzyl group at various stages of the synthesis and with several types of palladium catalysts was explored. In all cases, either no hydrogenolysis was observed or starting materials were recovered, suggesting that the triazole ring chelates to the palladium catalyst resulting in deactivation, or hydrogenation of the vinyl group occurred. Deprotection of 1-*p*-methoxybenzyl-4-vinyl-1,2,3-triazole, **18**, using concentrated H_2SO_4 was then examined and the desired unsubstituted derivative, **19**, obtained in low yield (22%). This low yield prompted examination of the pivaloyloxymethyl protecting group,¹⁶ for which the protected azide, as a precursor to 1-*H*-4-vinyl-1,2,3-triazole, was readily prepared from the commercially available chloromethylpivalate as outlined in Scheme 9. Mesylation of the triazole obtained from 3-butyn-1-ol gave the mesylate, **66**, which underwent elimination with NaI/DBU followed by removal of the pivalate group with NaOH to

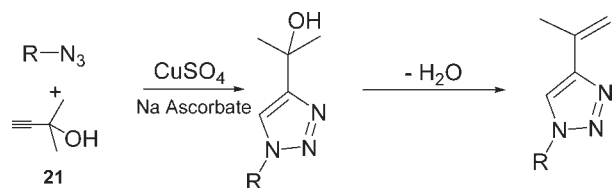
give a ca. 1:1 mixture of the desired product, **19**, and the 1-hydroxymethyl-4-vinyl-1,2,3-triazole, **20**. Separation of **19** and **20** proved difficult, however, treatment of this mixture with Dess-Martin reagent resulted in quantitative oxidative cleavage of **20** to yield essentially pure **19** in good yield. The 1-*H*-4-vinyl-1,2,3-triazole, **19**, was found to undergo facile autopolymerization during both isolation and storage at -20°C and requires the addition of radical inhibitors such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) during all facets of handling.

Synthesis of α -Methyl-4-vinyl-1,2,3-triazoles

The building block approach to vinyl triazole monomers not only allows the development of a variety of different synthetic strategies but also permits structural variations to be systematically incorporated into the vinyl triazole subunit. For instance, the synthesis of α -methyl-4-vinyl-1,2,3-triazole derivatives provides monomers for comparison of the physical and chemical properties of α -methyl-4-vinyl-1,2,3-triazoles with those of 4-vinyl-1,2,3-triazoles and their associated polymers, in a similar way to the widely examined styrenic versus α -methylstyrenic and acrylate versus methacrylate cases. The availability of both vinyl and α -methyl vinyl triazole monomers has significant implications from both an academic and industrial point of view and further increases the attractiveness of this new monomer family. The synthesis of the α -methyl derivatives was greatly facilitated by the availability of 2-methyl-3-butyn-2-ol, **21**,



Scheme 9. Synthesis of the parent 1-*H*-4-vinyl-1,2,3-triazole, **19**, by deprotection of 1-pivaloyloxymethyl-1,2,3-triazoles, **66**, followed by oxidative cleavage.



Scheme 10. Synthetic route for α -methyl-4-vinyl-1,2,3-triazoles.

which allowed direct cycloaddition with substituted azides to give the intermediate tertiary alcohol (Scheme 10). Reaction of the tertiary alcohol with mesyl chloride did not yield the mesylated 2-methyl-(1,2,3-triazol-4-yl)-ethan-2-ol derivative, instead the desired α -methyl vinyl compound was obtained in a single step regardless of the substituent on the triazole ring. Interestingly, other dehydration procedures such as POCl_3 /pyridine that proved unsuccessful for the 2-hydroxyethyl triazole derivatives were high yielding reactions in this case and led directly to the dehydrated product. For example, reaction of the benzyl derivative, $R = \text{benzyl}$, with POCl_3 /pyridine gave the α -methyl vinyl, **49**, in 98% yield after purification.

To further increase the availability of the α -methyl monomer family, the possibility of developing a one-pot click reaction starting from **21** and substituted alkyl halides was examined. As described previously, the compatibility of the Cu-catalyzed cycloaddition reaction with other reaction conditions allows sodium azide to be present which permits *in situ* generation of the alkyl azide. For example, reaction of methyl 3-bromopropionate with **21**, sodium azide, and copper sulfate gives the triazole derivative, **22**, which could be dehydrated in 90% yield with POCl_3 /pyridine to give the desired α -methyl derivative, **23** (Scheme 11).

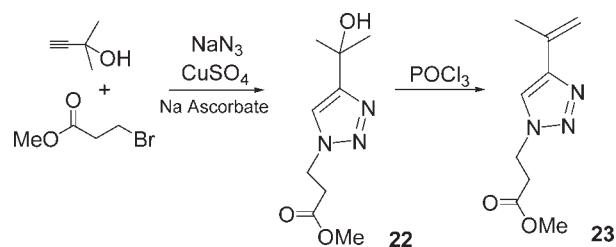
Characterization

The synthetic versatility associated with these “click”-based approaches to 4-vinyl-1,2,3-triazole monomers allows a wide variety of groups to be incorporated into the monomer structure, as illustrated in Figure 1. The generation of a diverse molecular library necessitates full characterization of these materials and the identification of distinctive spectroscopic features for the parent triazole ring. ^1H and ^{13}C NMR spectroscopy proved to be powerful in the analysis of these monomers with characteristic proton reso-

nances being observed at 7.5–8.5 ppm for the unique H-atom attached to the triazole ring (strong singlet). The presence of the triazole ring also gave rise to two singlets in the ^{13}C NMR spectra at ca. 122 and 126 ppm. These features can be observed in both the ^1H and ^{13}C (DEPT) NMR spectra for the hydroxyethyl substituted monomer, **45**, which shows a strong singlet for the triazole ring proton at 7.63 ppm and the characteristic set of resonances for a conjugated vinyl group and a hydroxyethyl substituent (Figure 2). The absence of other resonances in either spectrum demonstrates not only the high purity obtainable for these monomers but also the high degree of regioselectivity in the azide/alkyne coupling step and the complete absence of any 1,5-substituted triazole isomers. In select cases, the structure of the monomers was confirmed by X-ray crystallography which confirmed the 1,4-substitution pattern on the triazole ring as well as the introduction of the α -methyl group. Examples of single crystal structures for the hydroxyethyl derivative, **45**, and the benzyl, α -methyl analog, **49**, of benzyl methacrylate are shown in Figure 3.

CONCLUSIONS

In summary, a selection of synthetic approaches to the new monomer family based on 4-vinyl-1,2,3-triazole monomers have been developed. These approaches rely on the ready availability of both alkyne and alkyl halide starting materials. The mild nature of the approach, utilizing “click” followed by Wittig or elimination reactions, permits a wide range of derivatives with various functional groups to be prepared in high yields and demonstrates the significant structural versatility possible in these systems. It is anticipated that this new family of vinyl monomers will significantly extend the range of functional materials that can be prepared when



Scheme 11. Synthesis of 3-(4-(prop-1-en-2-yl)-1,2,3-triazole)-1-yl propanoate, **23**, by a one-pot azidation/click reaction, followed by dehydration.

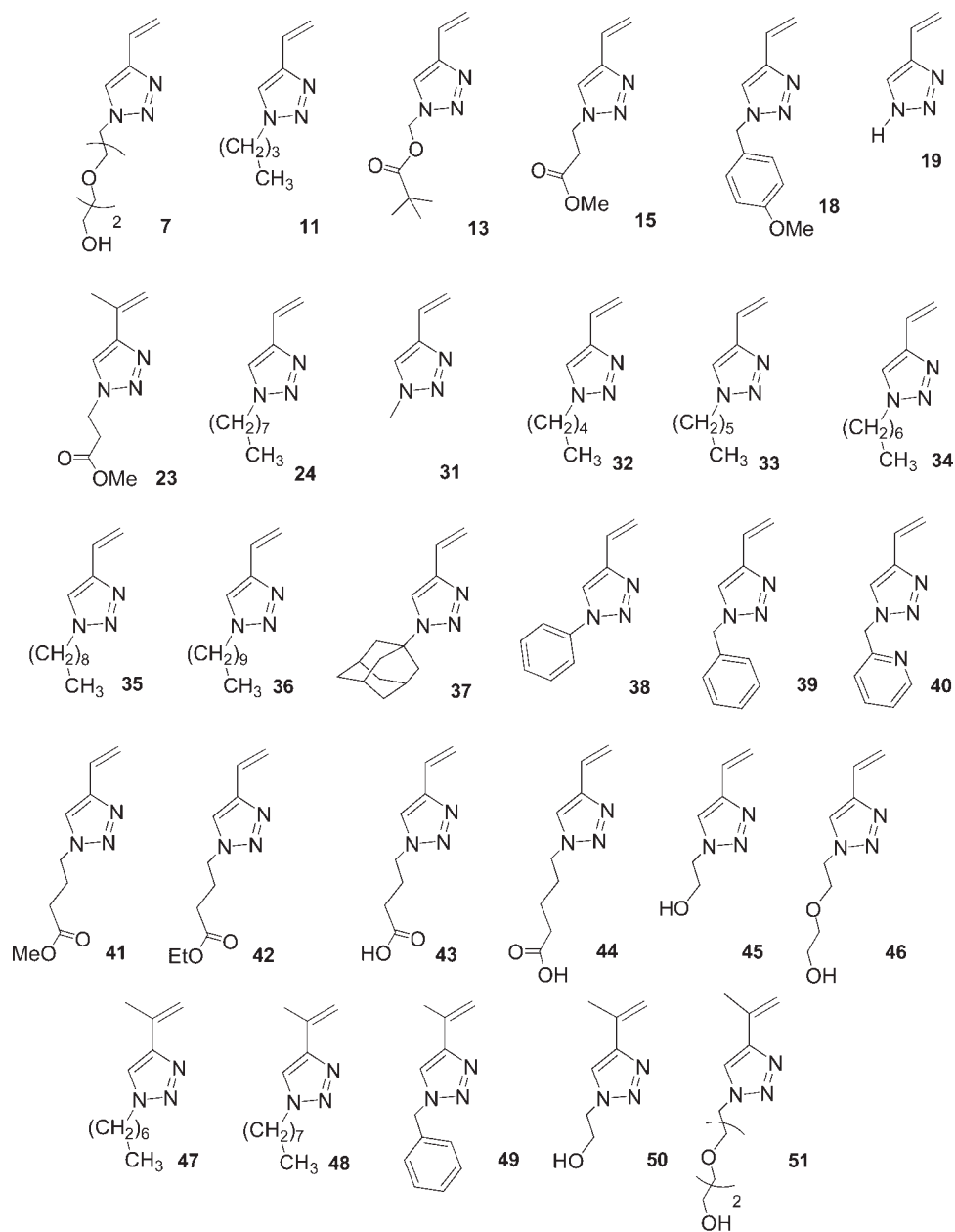


Figure 1. Range of 1,2,3-triazole monomers prepared by Cu-catalyzed azide/acetylene coupling reactions, followed by eliminations or Wittig reactions.

compared to traditional monomers such as styrene, vinylpyridine and meth/acrylates.

EXPERIMENTAL

General Procedures and Materials

All chemicals and solvents were purchased from Aldrich, of reagent grade, and used without further purification unless otherwise denoted below

and all reactions were carried out under air unless specified. Organic azides⁸ were synthesized according to established protocols. Analytical TLC was performed on commercial Merck plates coated with silica gel GF254 (0.24 mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230–400 mesh, ASTM). ¹H NMR (400 MHz and 200 MHz) and ¹³C NMR (100 MHz) measurements were performed on a Bruker AC 400 and 200 spectrometers at room temperature.

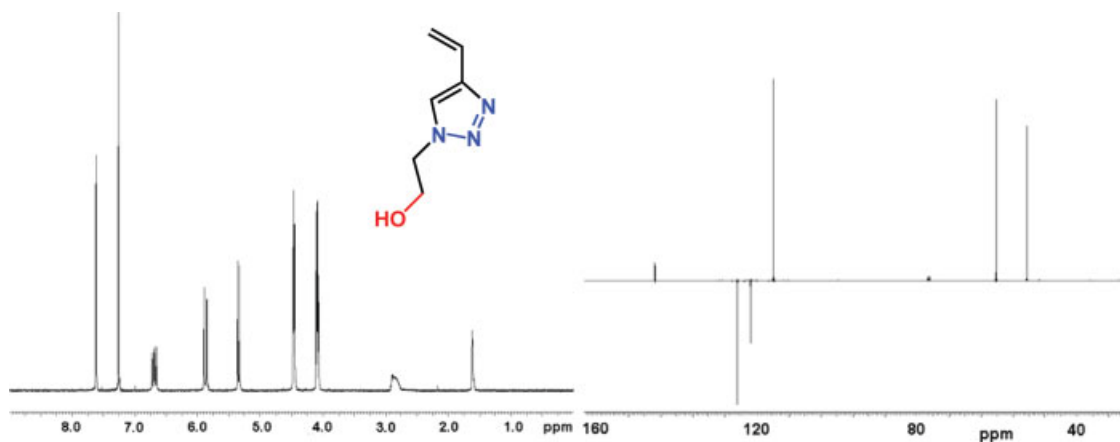


Figure 2. ^1H and ^{13}C NMR spectra of N-(2'-hydroxyethyl)-4-vinyl-1,2,3-triazole, **45**.

4-Trimethylsilyl-1-buten-3-yne (1)

To a two-neck flask equipped with a Dimroth condenser was added 200 mL of dry triethylamine. This solution was degassed with argon for 30 min before the addition of vinyl bromide (12.84 g, 120 mmol) and trimethylsilylacetylene (7.86 g, 80 mmol). The reaction mixture was subjected to a single freeze-pump-thaw cycle before adding CuI (152 mg, 0.80 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (281 mg, 0.40 mmol). After two additional freeze-pump-thaw cycles, the reaction mixture was stirred at room temperature overnight followed by addition of 200 mL of ether to the reaction mixture and the organic layer washed with ice cold 1 M NaHSO_4 (15 \times 200 mL), sat. NaHCO_3 (1 \times 200 mL), and brine (1 \times 200 mL). The ethereal layer was dried over MgSO_4 and concentrated. The product (bp 52–53 $^\circ\text{C}/80$ Torr) was distilled from the brown residue into a receiving flask cooled to -78 $^\circ\text{C}$. Yield: 6.43 g (67%) of a colorless liquid.

^1H NMR (400 MHz CDCl_3): 5.83 (dd, $J = 17.6, 11.1$ Hz, $\text{CH}_2=\text{CH}$, 1H), 5.69 (dd, $J = 17.6, 2.4$ Hz, *cis* $\text{CH}_2=\text{CH}$, 1H), 5.49 (dd, $J = 11.1, 2.4$ Hz, *trans* $\text{CH}_2=\text{CH}$, 1H), 0.19 (s, $\text{C}(\text{CH}_3)_3$, 9H). ^{13}C NMR (CDCl_3): δ 127.9, 117.2, 103.7, 95.0, -0.2 . Anal. Calcd for $(\text{C}_7\text{H}_{12}\text{Si})$: C, 67.66; H, 9.73. Found: C, 67.60; H, 9.72.

General procedure: Synthesis of Vinyl triazole Derivatives via the *In Situ* Generation of Vinyl acetylene. Synthesis of 1-Octyl-4-vinyl-1,2,3-triazole (**24**) Depicted

To a vigorously stirred solution of **1** (0.5 g, 4 mmol) and 1-azidooctane (0.94 g, 6.0 mmol) in

1:1 THF: H_2O was added sodium L-ascorbate (0.080 g, 0.40 mmol), CuSO_4 (0.032 g, 0.20 mmol), and 6 mL of tetrabutylammonium fluoride (1 M in THF). The reaction flask was then fitted with a rubber septum and allowed to stir overnight. The solution was concentrated and the product was extracted into 50 mL of dichloromethane (twice). The organic fractions were combined, dried over MgSO_4 , filtered, and concentrated under reduced pressure. Crude product was purified via flash column chromatography using 1:1 hexanes:ethyl acetate as eluent yielding 0.733 g (88%) of **24** as a clear oil.

^1H NMR (200 MHz, CDCl_3): δ 7.49 (s, ArH, 1H), 6.74 (dd, $J = 17.8, 11.2$ Hz, $\text{CH}_2=\text{CH}$, 1H), 5.86 (dd, $J = 17.8, 1.2$ Hz, *trans* $\text{CH}_2=\text{CH}$, 1H), 5.32 (dd, $J = 11.2, 1.4$ Hz, *cis* $\text{CH}_2=\text{CH}$, 1H), 4.33 (t, $J = 7.2$, NCH_2CH_2 , 2H), 1.89 (m, NCH_2CH_2 , 2H), 1.27 (m, $\text{NCH}_2\text{CH}_2[\text{CH}_2]_5\text{CH}_3$, 10H), 0.87 (t, $J = 13.8$ Hz, $\text{N}[\text{CH}_2]_7\text{CH}_3$ 3H). ^{13}C NMR (CDCl_3): δ 146.65 ($\text{NCH}=\text{C}$, 1C) 126.09

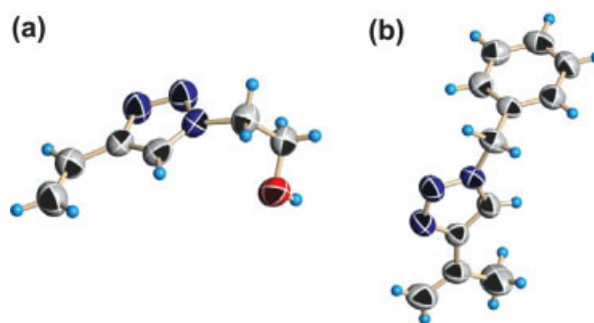


Figure 3. X-ray crystal structures for the triazole monomers, (a) N-(2'-hydroxyethyl)-4-vinyl-1,2,3-triazole, **45**, and (b) N-(benzyl)-4-(prop-1'-en-2'-yl)-1,2,3-triazole, **49**.

(CH=CH₂, 1C), 120.29 (NCH=C, 1C), 116.13 (CH=CH₂, 1C), 50.63 (NCH₂, 1C), 32.01 (NCH₂CH₂, 1C), 30.63 (N[CH₂]₂CH₂, 1C), 29.35 (N[CH₂]₃CH₂, 1C), 29.27 (N[CH₂]₄CH₂, 1C), 26.78 (N[CH₂]₅CH₂, 1C), 22.91 (N[CH₂]₆CH₂, 1C), 14.45 (N[CH₂]₇CH₃, 1C). Mass Spec for C₁₂H₂₁N₃ Calculated: 207.17; Found (M+H)⁺: 208.18.

Modified *In Situ* Generation of Vinyl acetylene Procedure: "One-Pot" Synthesis of 1-Methyl-4-vinyl-1,2,3-triazole (31) is Depicted

To a 20 mL scintillation vial was added sodium azide (1.95 g, 30.00 mmol), diisopropylethylamine (2.06 g, 15.94 mmol), and CuBr(PPh₃)₃ (943 mg, 1.00 mmol) and tetrabutylammonium fluoride (1 M in THF) (12 mL, 12.00 mmol). This heterogeneous mixture was then transferred via Pasteur pipette to a large glass ampule (100 mL) containing methyl iodide (1.42 g, 9.93 mmol) and **1** (1.00 g, 8.05 mmol) submerged in liquid nitrogen. The glass ampule was then subjected to a single freeze-pump-thaw cycle, sealed, and allowed to react for 16 h at 60 °C. On completion, the reaction mixture was concentrated under reduced pressure then partitioned into a separatory funnel containing 15 mL of deionized water and 15 mL of dichloromethane. The aqueous layer was extracted thrice more with 15 mL CH₂Cl₂. The organic fractions were then combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. Crude product was then purified via flash column chromatography using ethyl acetate as eluent yielding 0.60 g (68%) of **31** as a clear oil.

¹H NMR (200 MHz, CDCl₃): δ 7.49 (s, ArH, 1H), 6.65 (dd, *J* = 17.7, 11.2 Hz, CH=CH₂, 1H), 5.84 (d, *J* = 17.7 Hz, *trans* CH=CH₂, 1H), 5.31 (d, *J* = 11.2 Hz, *cis* CH=CH₂, 1H), 4.01 (s, NCH₃, 3H). ¹³C NMR (CDCl₃): δ 146.15 (Ar, NCH=C, 1C) 125.59 (CH=CH₂, 1C), 121.22 (NCH=C, 1C), 115.95 (CH=CH₂, 1C), 36.59 (NCH₃, 1C). Mass Spec for C₅H₇N₃ Calculated: 109.13; Found (M+H)⁺: 110.09.

General Procedure for Elimination Strategy Starting from But-3-yn-1-ol: Synthesis of 1-Octyl-4-vinyl-1,2,3-triazole (24) Depicted

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 1-azidooctane (1.01 g, 6.51 mmol), 3-butyn-1-ol, **2**, (0.47 g, 6.7 mmol), and 10 mL of *t*-butanol. In separate

flasks, sodium L-ascorbate (0.13 g, 0.64 mmol) and CuSO₄ (0.05 g, 0.32 mmol) were introduced to 5 mL of deionized water respectively. On dissolution, these aqueous solutions were then added to the *t*-butanol mixture. After 13 h of vigorous stirring, the reaction mixture was poured into a separatory funnel containing 80 mL of deionized water and extracted four times with 80 mL of CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (ethyl acetate) to yield 1.47 g (100%) of 2-(1-octyl-1*H*-1,2,3-triazol-4-yl) ethanol, **52**, as a white solid.

¹H NMR (200 MHz, CDCl₃): 7.36 (s, ArH, 1H), 4.32 (t, *J* = 7.3 Hz, NCH₂, 2H), 3.95 (t, *J* = 5.9 Hz, OCH₂CH₂, 2H), 2.95 (t, *J* = 5.8 Hz, OCH₂CH₂, 2H), 1.89 (m, OH, NCH₂CH₂, 3H), 1.28 (m, NCH₂CH₂[CH₂]₅CH₃, 10H), 0.88 (m, N[CH₂]₇CH₃, 3H). ¹³C NMR (CDCl₃): δ 145.65 (NCH=C, 1C), 121.52 (NCH=C, 1C), 61.79 (OCH₂CH₂, 1C), 50.45 (NCH₂, 1C), 31.86 (N[CH₂]₅CH₂, 1C), 30.46 (NCH₂CH₂, 1C), 29.19 (N[CH₂]₃CH₂, 1C), 29.12 (N[CH₂]₄CH₂, 1C), 28.87 (OCH₂CH₂, 1C), 26.67 (N[CH₂]₂CH₂, 1C), 22.75 (N[CH₂]₆CH₂, 1C), 14.22 (N[CH₂]₇CH₃, 1C). Mass Spec for C₁₂H₂₃N₃O Calculated: 225.18; Found (M): 225.18. These hydroxyl compounds could be used without further characterization.

To a 20 mL scintillation vial was added **52** (0.14 g, 0.64 mmol), NEt₃ (0.19 g, 19.1 mmol), and 6 mL of CH₂Cl₂. After cooling the vial to 0 °C, methanesulfonyl chloride (0.12 g, 1.03 mmol) was added dropwise and stirred at 0 °C, then the reaction mixture was allowed to warm to room temperature gradually. After 13 h of vigorous stirring, the reaction mixture was poured into a separatory funnel containing 10 mL of CH₂Cl₂ and washed with 1 M HCl and Brine. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure to yield 0.18 g (95%) of 2-(1-octyl-1*H*-1,2,3-triazol-4-yl)ethyl methanesulfonate, **53**, as a white solid.

¹H NMR (200 MHz, CDCl₃): 7.43 (s, ArH, 1H), 4.53 (t, *J* = 6.4 Hz, OCH₂CH₂, 2H), 4.33 (t, *J* = 7.3 Hz, NCH₂, 2H), 3.19 (t, *J* = 6.4 Hz, OCH₂CH₂, 2H), 2.97 (s, CH₃S, 3H), 1.89 (m, NCH₂CH₂, 2H), 1.26 (m, NCH₂CH₂(CH₂)₅CH₃, 10H), 0.88 (m, N(CH₂)₇CH₃, 3H). Mesylated compounds were utilized without further characterization unless otherwise denoted.

A 5 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with **53** (0.030 g, 0.11 mmol) and glyme (1.00 g, 1.15 mL) to make a 0.1 M solution of **53**. To this mixture was added NaI (0.05 g, 0.34 mmol) followed by DBU (0.03 g, 0.23 mmol). After addition of all reagents, reaction was heated to reflux for a period of 30 min. On completion, reaction mixture was partitioned between CH₂Cl₂ and water and the aqueous layer extracted three times with CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 0.020 g (79%) of **24** as a clear oil.

¹H NMR (200 MHz, CDCl₃): 7.49 (s, ArH, 1H), 6.74 (dd, *J* = 17.8, 11.2 Hz, CH₂=CH, 1H), 5.86 (dd, *J* = 17.8, 1.2 Hz, *cis* CH₂=CH, 1H), 5.32 (dd, *J* = 11.2, 1.4 Hz, *trans* CH₂=CH, 1H), 4.33 (t, *J* = 7.2 Hz, NCH₂CH₂, 2H), 1.89 (m, NCH₂CH₂, 2H), 1.27 (m, NCH₂CH₂[CH₂]₅CH₃, 10H), 0.87 (t, *J* = 6.9 Hz, N[CH₂]₇CH₃, 3H). ¹³C NMR (CDCl₃): 146.65 (NCH=C, 1C), 126.09 (CH=CH₂, 1C), 120.29 (NCH=C, 1C), 116.13 (CH=CH₂, 1C), 50.63 (NCH₂, 1C), 32.01 (NCH₂CH₂, 1C), 30.63 (N[CH₂]₂CH₂, 1C), 29.35 (N[CH₂]₃CH₂, 1C), 29.27 (N[CH₂]₄CH₂, 1C), 26.78 (N[CH₂]₅CH₂, 1C), 22.91 (N[CH₂]₆CH₂, 1C), 14.45 (N[CH₂]₇CH₃, 1C). Mass Spec for C₁₂H₂₁N₃. Calculated: 207.17; Found (M+H)⁺: 208.18.

Elimination Reaction of 2-(1-Octyl-1*H*-1,2,3-triazol-4-yl)ethyl methanesulfonate (**53**) Using *t*-BuOK

A 5 mL round bottom flask equipped with a magnetic stir bar was charged with **53** (0.040 g, 0.12 mmol) and *t*-BuOH (3.09 g, 3.99 mL). To this mixture was added *t*-BuOK (0.06 g, 0.50 mmol) and 18-Crown-6 (0.13 g, 0.49 mmol). After addition of all reagents, reaction was heated to 50 °C for a period of 1 h. On completion, the reaction mixture was partitioned between CH₂Cl₂ and water and the aqueous layer extracted three times with CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 0.022 g (83%) of **24** as a clear oil.

General Procedure for Elimination Strategy Using Protecting Groups: Synthesis of 2-(2-(2-(4-Vinyl-1,2,3-triazole-1-yl))ethoxy)ethoxyethanol (**7**) Depicted

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 2-(2-(2-azido)ethoxy)ethoxyethanol (0.50 g, 2.86 mmol), 3,4-dihydro-2*H*-pyran (0.36 g, 4.28 mmol), CH₂Cl₂ (26.50 g, 20.08 mL), and pyridinium *p*-toluenesulfonate (0.08 g, 0.33 mmol). After 4 h of vigorous stirring, the reaction mixture was poured into a separatory funnel containing 80 mL of deionized water and extracted four times with 80 mL of Et₂O. The organic fractions were combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 0.50 g (71%) of protected azide, **3**, as a colorless oil.

¹H NMR (200 MHz, CDCl₃): 4.64 (t, *J* = 3.3 Hz, OCH(CH₂)O, 1H), 3.94–3.37 (m, OCH₂, 14H), 1.95–1.47 (m, cyclic-CH₂, 6H). This protected azide was utilized without further characterization.

“Click reaction” with 3-butyn-1-ol, **2**, followed by mesylation reaction and elimination reaction were conducted by using the similar method depicted above for **24** to yield the protected 4-vinyl-1,2,3-triazole, **6**, as a slightly yellow oil (53% yield for 3 steps).

¹H NMR (200 MHz, CDCl₃): 7.73 (s, ArH, 1H), 6.74 (dd, *J* = 17.8, 11.1 Hz, CH₂=CH, 1H), 5.86 (dd, *J* = 17.8, 1.5 Hz, *trans* CH₂=CH, 1H), 5.32 (dd, *J* = 11.1, 1.3 Hz, *cis* CH₂=CH, 1H), 4.60 (b, OCH(CH₂)O, 1H), 4.52 (t, *J* = 5.2, cyclic-OCH₂CH₂, 2H), 3.89–3.43 (m, OCH₂, 12H), 1.95–1.47 (m, cyclic-CH₂, 6H). This compound was utilized without further characterization.

To a 20 mL scintillation vial were added THF (0.54 g, 0.06 mL), acetic acid (1.26 g 1.20 mL), and 0.3 mL of H₂O. Then **6** (0.060 g, 0.19 mmol) was added and heated to 50 °C for a period of 4 h. On completion, the reaction mixture was concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 0.040 g (91%) of **7** as a white solid.

¹H NMR (200 MHz, CDCl₃): 7.70 (s, ArH, 1H), 6.69 (dd, *J* = 17.8, 12.6 Hz, CH=CH₂, 1H), 5.85 (dd, *J* = 17.8, 1.4 Hz, *trans* CH=CH₂, 1H), 5.30 (dd, *J* = 12.6, 1.4 Hz, *cis* CH=CH₂, 1H), 4.50 (t, *J* = 5.2 Hz HOCH₂, 2H), 3.85 (t, *J* = 5.2 Hz, HOCH₂CH₂, 2H), 3.72–3.51 (m, OCH₂CH₂,

8H), 2.50 (s, OH). ^{13}C NMR (CDCl_3): δ 146.51 (NCH=C, 1C), 125.89 (CH=CH₂, 1C), 121.72 (NCH=C, 1C), 116.11 (CH=CH₂, 1C), 72.61 (NCH₂, 1C), 70.80 (NCH₂CH₂, 1C), 70.40 (N(CH₂)₂OCH₂, 1C), 69.67 (N(CH₂)₂OCH₂CH₂, 1C), 61.90 (N[(CH₂)₂O]₂CH₂, 1C), 50.39 (CH₂CH₂OH, 1C). Mass Spec for C₁₀H₁₇N₃O₃ Calculated: 227.13; Found (M+H)⁺: 228.13.

Modified Procedure for Elimination Strategy Starting from But-3-yn-1-ol and Employing a "One-Pot 'Click' Reaction": Synthesis of 1-Butyl-4-vinyl-1,2,3-triazole (11) Depicted

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with NaN₃ (4.25 g, 65.30 mmol), CuSO₄ (0.34 g, 2.16 mmol), sodium L-ascorbate (1.46 g, 7.39 mmol), DMF (9.45 g, 10 mL), and 10 mL of H₂O. Then 3-butyn-1-ol, **2**, and 1-bromobutane were added and heated to 60 °C. After 15 h of vigorous stirring, the reaction mixture was cooled to room temperature and the reaction mixture filtered through celite, the celite cake washed with MeOH, and the organic extracts concentrated under reduced pressure. The resulting crude mixture was then purified via flash column chromatography (ethyl acetate) to yield 1.75 g (47%) of 2-(1-butyl-1H-1,2,3-triazol-4-yl)ethanol, **9**, as a clear oil.

^1H NMR (200 MHz, CDCl_3): 7.35 (s, ArH, 1H), 4.15 (t, $J = 7.1$ Hz, NCH₂, 2H), 3.73 (b, OCH₂CH₂, 2H), 2.79 (b, OCH₂CH₂, 2H), 1.70 (t, $J = 7.0$ Hz, NCH₂CH₂, 2H), 1.17 (m, NCH₂CH₂CH₂CH₃, 2H), 0.76 (t, $J = 7.1$ Hz, N[CH₂]₃CH₃, 3H). ^{13}C NMR (CDCl_3): 145.19 (NCH=C, 1C), 121.62 (NCH=C, 1C), 61.08 (OCH₂CH₂, 1C), 49.75 (NCH₂, 1C), 32.02 (NCH₂CH₂, 1C), 28.78 (OCH₂CH₂, 1C), 19.48 (N[CH₂]₂CH₂, 1C), 13.26 (N[CH₂]₃CH₃, 1C). Mass Spec for C₈H₁₅N₃O Calculated: 169.24; Found (M+H)⁺: 170.23.

The mesylation of **9** followed by elimination was conducted by using the similar method depicted earlier for **24** to yield **11** as a clear oil (58% overall yield for 2 steps).

^1H NMR (200 MHz, CDCl_3): 7.48 (s, ArH, 1H), 6.57 (dd, $J = 17.8, 11.2$ Hz, CH=CH₂, 1H), 5.85 (dd, $J = 17.6, 1.2$ Hz, *trans* CH=CH₂, 1H), 5.17 (d, $J = 11.0$ Hz, *cis* CH=CH₂, 1H), 4.19 (t, $J = 7.2$ Hz, NCH₂, 2H), 1.73 (m, NCH₂CH₂, 2H), 1.22 (m, NCH₂CH₂CH₂CH₃, 2H), 0.79 (t, $J = 7.2$ Hz, N[CH₂]₃CH₃, 3H). ^{13}C NMR (CDCl_3): 146.08 (NCH=C, 1C), 125.67 (CH=CH₂, 1C), 120.22 (NCH=C, 1C), 115.53 (CH=CH₂, 1C),

49.82 (NCH₂, 1C), 32.10 (NCH₂CH₂, 1C), 19.49 (N[CH₂]₂CH₂, 1C), 13.29 (N[CH₂]₃CH₃, 1C). Mass Spec for C₈H₁₃N₃ Calculated: 151.23; Found (M+H)⁺: 152.24.

Synthesis of But-3-ynyl methanesulfonate (8)

To a 250 mL round bottom flask charged with a magnetic stir bar and 90 mL of CH₂Cl₂, 3-butyn-1-ol, **2**, (0.50 g, 7.13 mmol), and triethylamine (2.17 g, 21.40 mmol) were added. After cooling this mixture in an ice bath, methanesulfonyl chloride (1.06 g, 9.23 mmol) was added dropwise over 30 min. The reaction mixture was then allowed to warm to room temperature and was allowed to react overnight (16 h). On completion, the reaction mixture was washed with 1 M aqueous HCl and brine. The organic extract was then dried over MgSO₄, filtered, and concentrated under reduced pressure to yield 1.02 g (96%) of **8** as an orange oil.

^1H NMR (200 MHz, CDCl_3): 4.23 (t, $J = 6.6$ Hz, OCH₂CH₂, 2H), 3.00 (s, CH₃S, 3H), 2.59 (dt, $J = 6.6, 2.6$ Hz, OCH₂CH₂CCH, 2H), 2.05 (t, $J = 2.6$ Hz, CH₂CCH, 1H). ^{13}C NMR (CDCl_3): 78.83 (HCCCH₂, 1C), 71.03 (HCCCH₂, 1C), 67.36 (CH₂CH₂O, 1C), 37.50 (SCH₃, 1C), 19.63 (CH₂CH₂O, 1C). Mass Spec for C₅H₈N₃O₃S Calculated: 148.02; Found (M+H)⁺: 149.04.

General Procedure for Elimination Strategy Starting from Mesylated Alkyne Derivatives: Synthesis of 1-Octyl-4-vinyl-1,2,3-triazole (24) Depicted

A 250 mL round bottom flask equipped with a magnetic stir bar was charged with 1-azidooctane (3.53 g, 20.30 mmol), **8** (3.05 g, 20.30 mmol), and 30 mL of *t*-butanol. In separate flasks, sodium ascorbate (1.20 g, 0.61 mol) and CuSO₄ (0.16 g, 0.1 mmol) was introduced to 15 mL of deionized water respectively. On dissolution, these aqueous mixtures were then added to the *t*-butanol mixture. After 16 h of vigorous stirring, the reaction mixture was concentrated under reduced pressure. The resulting aqueous mixture was then extracted three times with CH₂Cl₂ (30 mL). The organic fractions were combined, dried over MgSO₄, filtered and concentrated under reduced pressure and was further purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 5.61 g (86%) of **53** as a white solid.

^1H NMR (200 MHz, CDCl_3): δ 7.43 (s, ArH, 1H), 4.53 (t, $J = 6.4$ Hz, OCH_2CH_2 , 2H), 4.33 (t, $J = 7.3$ Hz, NCH_2 , 2H), 3.19 (t, $J = 6.4$ Hz, OCH_2CH_2 , 2H), 2.97 (s, CH_3S , 3H), 1.89 (m, NCH_2CH_2 , 2H), 1.26 (m, $\text{NCH}_2\text{CH}_2[\text{CH}_2]_5\text{CH}_3$, 10H), 0.88 (m, $\text{N}[\text{CH}_2]_7\text{CH}_3$, 3H). Mesylated compounds were utilized without further characterization unless otherwise denoted.

The elimination reaction of **53** to yield **24** was conducted in exactly the same way as described earlier.

General Procedure for Elimination Strategy Starting from 3-Butyn-2-ol: Synthesis of 1-Benzyl-4-vinyl-1,2,3-triazole (**39**) Depicted

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with benzylazide (2.00 g, 14.27 mmol), 3-butyn-2-ol (1.02 g, 14.50 mmol), and 25.8 mL of *t*-butanol. In separate flasks, sodium L-ascorbate (0.85 g, 4.28 mmol) and CuSO_4 (0.23 g, 1.43 mmol) were introduced to 25.8 mL of deionized water, respectively. On dissolution, these aqueous solutions were then added to the *t*-butanol mixture. After overnight of vigorous stirring, the reaction mixture was poured into a separatory funnel containing 200 mL of deionized water and extracted four times with 200 mL of CH_2Cl_2 . The organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (ethyl acetate) to yield 2.67 g (85%) of 1-(1-benzyl-1,2,3-triazol-4-yl)ethanol, **56**, as a white solid.

^1H NMR (200 MHz, CDCl_3): 7.41 (s, Ar(triazole)H, 1H), 7.35–7.10 (m, Ar(benzene)H, 5H), 5.38 (s, NCH_2C , 2H), 4.97 (q, HOCHCH_3C , 1H), 4.40 (b, OH, 1H), 1.45 (d, CH_3 , 1H). ^{13}C NMR (CDCl_3): 153.08 ($\text{NCH}=\text{C}$, 1C), 134.73 (Ar, CH_2C , 1C), 129.04 (*m*-Ar, 2C), 128.64 (*p*-Ar, 1C), 128.08 (*o*-Ar, 2C), 120.48 ($\text{NCH}=\text{C}$, 1C), 62.72 (HOCHCH_3C , 1C), 54.03 (NCH_2 , 1C), 23.21 (CH_3 , 1C). Mass Spec for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$ Calculated: 203.11; Found ($\text{M}+\text{H}$) $^+$: 204.10.

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **56** (0.27 g, 1.35 mmol), *p*-toluenesulfonic acid monohydrate (0.01 g, 0.04 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (about 0.0001 g), and 4.5 mL of DMSO. The reaction mixture was then heated at 140 °C with stirring for 1.5 h and then poured into a separatory funnel containing 100 mL of saturated $\text{NaHCO}_3\text{aq.}$ and extracted four

times with 100 mL of CH_2Cl_2 . The organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 0.23 g (86%) of 1-benzyl-4-vinyl-1H-1,2,3-triazole, **39**, as a white solid.

^1H NMR (200 MHz, CDCl_3): 7.39–7.24 (s, ArH, 6H), 6.69 (dd, $J = 17.8, 11.2$ Hz, $\text{CH}=\text{CH}_2$, 1H), 5.85 (dd, $J = 17.8, 1.2$ Hz, *trans* $\text{CH}=\text{CH}_2$, 1H), 5.51 (s, NCH_2 , 2H), 5.30 (dd, $J = 11.2, 1.0$ Hz, *cis* $\text{CH}=\text{CH}_2$, 1H). ^{13}C NMR (CDCl_3): 146.98 ($\text{NCH}=\text{C}$, 1C), 134.80 (Ar, NCH_2C , 1C), 129.31 (*o*-Ar, 2C), 128.95 ($\text{CH}=\text{CH}_2$, 1C), 128.23 (*m*-Ar, 2C), 125.78 (*p*-Ar, 1C), 120.28 ($\text{CH}=\text{CH}_2$, 1C), 116.04 ($\text{NCH}=\text{C}$, 1C), 54.29 (NCH_2 , 1C). Mass Spec for $\text{C}_{11}\text{H}_{11}\text{N}_3$ Calculated: 185.23; Found ($\text{M}+\text{H}$) $^+$: 186.22.

General Procedure for Wittig Reaction via Aldehyde Substituted Triazole Intermediate: Synthesis of 1-(4-Methoxybenzyl)-4-vinyl-1,2,3-triazole (**18**) Depicted

A 500 mL round bottom flask equipped with a magnetic stir bar was charged with 4-methoxybenzylazide (9.15 g, 56.08 mmol), propargyl alcohol (3.64 g, 6.69 mmol), and 100 mL of *t*-butanol. In separate flasks, sodium L-ascorbate (3.72 g, 18.79 mmol) and CuSO_4 (0.51 g, 3.21 mmol) were introduced to 50 mL of deionized water, respectively. On dissolution, these aqueous solutions were then added to the *t*-butanol mixture. After 3 nights of vigorous stirring, the reaction mixture was poured into a separatory funnel containing 400 mL of deionized water and extracted four times with 500 mL of CH_2Cl_2 . The organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. This crude mixture was then purified via gradient flash column chromatography (ethyl acetate to MeOH) to yield 10.80 g (88%) of 1-(4-methoxybenzyl)-4-hydroxymethyl-1,2,3-triazole, **17**, as a white solid.

^1H NMR (200 MHz, CDCl_3): 7.41 (s, Ar(triazole)H, 1H), 7.23 (d, $J = 6.6$ Hz, Ar(benzene-*ortho*)H 2H), 6.89 (d, $J = 6.6$ Hz, Ar(benzene-*meta*)H 2H), 5.45 (s, NCH_2C , 2H), 4.75 (s, OCH_2C , 2H), 3.80 (s, OCH_3 , 3H), 2.01 (s, OH, 1H). ^{13}C NMR (CDCl_3): 160.06 (CH_3OC , 1C), 148.28 ($\text{NCH}=\text{C}$, 1C), 129.87 (*o*-Ar, 2C), 126.63 (Ar, CCH_2C , 2C), 121.68 ($\text{NCH}=\text{C}$, 1C), 114.61 (*m*-Ar, 2C), 56.35 (OCH_2C , 1C), 55.49 (CH_3O , 1C), 53.86 (NCH_2 , 1C). Mass Spec for

$C_{11}H_{13}N_3O_2$ Calculated: 219.10; Found (M): 219.10.

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **17** (0.29 g, 1.34 mmol), triphenylphosphine (0.38 g, 1.46 mmol), and 3.30 mL of CH_2Cl_2 . Cooled this mixture to 0 °C and *N*-bromosuccinimide (0.28 g, 1.55 mmol) was added under argon atmosphere. After 3 h of vigorous stirring, the reaction mixture was concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (ethyl acetate) to yield 0.34 g (90%) of 1-(4-methoxybenzyl)-4-bromomethyl-1,2,3-triazole, **55**, as a white solid.

1H NMR (200 MHz, $CDCl_3$): 7.44 (s, Ar(triazole)H, 1H), 7.24 (d, $J = 9.0$ Hz, Ar(benzene-ortho)H 2H), 6.91 (d, $J = 9.0$ Hz, Ar(benzene-meta)H 2H), 5.45 (s, NCH_2C , 2H), 4.54 (s, $BrCH_2C$, 2H), 3.81 (s, OCH_3 , 3H). ^{13}C NMR ($CDCl_3$): 160.22 (CH_3OC , 1C) 145.04 ($NCH=C$, 1C), 129.98 (*o*-Ar, 2C), 126.31 (Ar, CH_2C , 1C), 122.67 ($NCH=C$, 1C), 114.74 (*m*-Ar, 2C), 55.54 (CH_3O , 1C), 54.08 (NCH_2 , 1C), 21.83 ($BrCH_2$, 1C). Mass Spec for $C_{11}H_{12}BrN_3O$ Calculated: 281.02; Found (M): 281.02.

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with **55** (0.34 g, 1.20 mmol), triphenylphosphine (0.32 g, 1.20 mmol), and 2.30 mL of CH_2Cl_2 . After 40 h of vigorous stirring, the reaction mixture was concentrated under reduced pressure. Hexanes were added to this resulting crude mixture and then decanted off to yield 0.56 g (86%) of phosphineylide, **56**, as a pale yellow solid.

1H NMR (200 MHz, $CDCl_3$): δ 8.29 (s, Ar(triazole)H, 1H), 7.80–7.48 (m, Ar(triphenylphosphine)H 15H), 7.04 (d, $J = 8.6$ Hz, Ar(benzene-ortho)H 2H), 7.04 (d, $J = 8.6$ Hz, Ar(benzene-meta)H 2H), 5.48 (d, $J = 13.6$ Hz, PCH_2C , 2H), 5.26 (s, NCH_2C , 2H), 3.75 (s, OCH_3 , 3H). Mass Spec for $C_{29}H_{27}BrN_3OP$ Calculated: 543.11; Found (M): 464.19 (only cationic moiety). This compound was utilized without further characterization.

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with **56** (0.25 g, 0.46 mmol), 37% aqueous HCHO (0.10 g, 1.21 mmol) was dissolved into 0.49 mL of H_2O and then added 0.31 mL of hexanes and 0.85 mL of CH_2Cl_2 . Ten molar aqueous NaOH (0.17 g) was then added dropwise to this mixture. After 14 h of vigorous stirring, the reaction mixture was poured into a separatory funnel containing

10 mL of 1 M HCl and extracted four times with 10 mL of CH_2Cl_2 . The organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 0.08 g (84%) of **18** as a white solid.

1H NMR (200 MHz, $CDCl_3$): 7.40 (s, Ar(triazole)H, 1H), 7.23 (d, $J = 6.8$ Hz, Ar(benzene-ortho)H 2H), 6.90 (d, $J = 6.8$ Hz, Ar(benzene-meta)H 2H), 6.69 (dd, $J = 18.0, 10.6$ Hz, $CH_2=CH$ 1H), 5.85 (d, $J = 18.0$ Hz, *trans* $CH=CH_2$, 1H), 5.44 (s, NCH_2C , 2H), 5.31 (d, $J = 10.6$ Hz, *cis* $CH=CH_2$, 1H), 3.81 (s, OCH_3 , 3H), 2.01 (s, OH, 1H). ^{13}C NMR ($CDCl_3$): 160.10 (CH_3OC , 1C) 146.87 ($NCH=C$, 1C), 129.82 (*o*-Ar, 2C), 126.75 (Ar, CH_2C , 2C), 125.84 ($CH_2=CH$, 1C), 120.05 ($NCH=C$, 1C), 116.19 ($CH_2=CH$, 1C), 114.65 (*m*-Ar, 2C), 55.51 (CH_3O , 1C), 53.82 (NCH_2 , 1C). Mass Spec for $C_{12}H_{13}N_3O$ Calculated: 215.06; Found (M+H)⁺: 216.07.

Synthesis of 1-Unsubstituted 4-Vinyl-1,2,3-triazole (**19**) from 1-(4-Methoxybenzyl)-4-vinyl-1,2,3-triazole (**18**)

A 500 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with 1-(4-methoxybenzyl)-4-vinyl-1,2,3-triazole, **18**, (35.01 g, 0.16 mmol), 4-methoxyphenol (MEHQ) as a radical inhibitor (0.001 g), and 165 g of conc. H_2SO_4 . After 1 h of vigorous stirring at refluxing condition, the reaction mixture was cooled to 0 °C. By adding NaOH and deionized water, the pH of the reaction mixture was adjusted to ~ 3 and the reaction mixture poured into a separatory funnel and extracted 4 times with 300 mL of CH_2Cl_2 . The organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 3.43 g (22%) of **19** as a clear oil.

1H NMR (200 MHz, $CDCl_3$): 7.79 (s, ArH, 1H), 6.79 (dd, $J = 17.8, 11.2$ Hz, $CH=CH_2$, 1H), 5.92 (dd, $J = 17.8, 0.8$ Hz, *trans* $CH=CH_2$, 1H), 5.47 (dd, $J = 11.2, 0.8$ Hz, *cis* $CH=CH_2$, 1H). ^{13}C NMR ($CDCl_3$): 143.57 ($NHCH=C$, 1C), 127.50 ($NHCH=C$, 1C), 124.06 ($CH=CH_2$, 1C), 117.96 ($CH=CH_2$, 1C). Mass Spec for $C_4H_5N_3$ Calculated: 95.05; Found (M): 95.07. (This 1-unsubstituted

4-vinyl-1,2,3-triazole, **19**, tends to auto-polymerize readily and storing in freezer in the presence of radical inhibitor is required.)

Synthesis of 1-Unsubstituted 4-Vinyl-1,2,3-triazole (**19**) from (4-Vinyl-1,2,3-triazol-1-yl)methyl pivalate (**13**)

A 2 L round bottom flask equipped with a magnetic stir bar and was charged with mixture of (4-vinyl-1,2,3-triazol-1-yl)methyl pivalate, **13-A**, (7.16 g, 34.20 mmol) and (4-vinyl-1,2,3-triazol-2-yl)methyl pivalate, **13-B**, (8.95 g, 42.80 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical inhibitor (0.003 g), 730 mL of MeOH and 240 mL of deionized water. Then NaOH (6.57 g, 164.25 mmol) was added and after 30 min of vigorous stirring 1 M aqueous HCl added so that the pH of the reaction mixture was adjusted to ca. 3. Then the reaction mixture was poured into a separatory funnel and extracted four times with 800 mL of CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered and concentrated under reduced pressure. This crude mixture mainly includes **19** and 1-hydroxymethyl-4-vinyl-1,2,3-triazole, **20**, (Calculated from ¹H NMR, 2.45 g (25.70 mmol, 33% yield) of **19** and 3.12 g (24.90 mmol, 32% yield) of **20** were contained respectively) was used without further purification.

¹H NMR (200 MHz, CDCl₃) of **20**: 7.73 (s, ArH, 1H), 7.26 (b, OH), 6.73 (dd, *J* = 17.8, 11.2 Hz, CH=CH₂, 1H), 5.89 (dd, *J* = 17.8, 1.0 Hz, *trans* CH=CH₂, 1H), 5.79 (s, NCH₂OH), 5.47 (dd, *J* = 11.2, 1.0 Hz, *cis* CH=CH₂, 1H).

A 2 L round bottom flask equipped with a magnetic stir bar and was charged with this crude mixture (2.45 g (25.70 mmol) of **19** and 3.12 g (24.90 mmol) of **20**), Dess-Martin periodinane (17.75 g, 41.85 mmol) and 150 mL of CH₂Cl₂. After 21 h of vigorous stirring, the reaction mixture was poured into a separatory funnel containing 300 mL of deionized water and 150 mL of CH₂Cl₂. Then by adding 1 M aqueous HCl, the pH of the aqueous layer was adjusted to ~ 3 and extracted four times with 300 mL of CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting crude mixture was purified via flash column chromatography (1:1 ethyl acetate:hexanes) to yield 4.45 g (93% from mixture of **19** and **20**) of **19** as a light yellow oil.

General Procedure for Synthesis of α -Methylvinyl triazole Derivatives by an Elimination Strategy. Synthesis of 1-Benzyl-4-(prop-1-en-2-yl)-1,2,3-triazole (**49**) is Depicted

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with benzylazide (4.12 g, 30.91 mmol), 2-methyl-3-butyn-2-ol (2.60 g, 30.91 mmol), and 38 mL of *t*-butanol. In separate flasks, sodium L-ascorbate (0.18 g, 0.93 mmol) and CuSO₄ (0.05 g, 0.31 mmol) were introduced to 19 mL of deionized water, respectively. On dissolution, these aqueous solutions were then added to the *t*-butanol mixture. After 20 h of vigorous stirring at room temperature, the reaction mixture was poured into a separatory funnel containing 70 mL of deionized water and extracted three times with 70 mL of CH₂Cl₂. The organic fractions were washed once with deionized water, then combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (ethyl acetate) to yield 4.75 g (71%) of 1-benzyl-4-(2'-hydroxypropan-2'-yl)-1,2,3-triazole, **57**, as a white solid.

¹H NMR (200 MHz, CDCl₃): 7.37–7.20 (s, ArH, 6H), 5.47 (s, NCH₂CH, 2H), 1.60 (s, C(CH₃)₂OH, 6H). These hydroxyl compounds were utilized without further characterization.

To a 100 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was added **57** (4.70 g, 21.60 mmol) and pyridine (45 g) at room temperature. After stirring for 5 min, POCl₃ (6.63 g, 43.20 mmol) was added dropwise over 5 min at 0 °C. The reaction mixture was then brought to 120 °C and allowed to reflux for 2 h. On completion, the reaction mixture was poured over ice and CH₂Cl₂ and aqueous layer was washed with 1 M aqueous HCl and satd. Aqueous NaHCO₃. The organic fraction was dried over MgSO₄, filtered and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (ethyl acetate) to yield 4.20 g (98%) of **49** as a white solid.

¹H NMR (200 MHz, CDCl₃): 7.41 (s, ArH(triazole), 1H), 7.37–7.22 (s, ArH(benzene), 5H) 5.67 (s, *cis*(to CH₃) CH₂=CCH₃, 1H), 5.50 (s, NCH₂C, 2H), 5.06 (m, *trans*(to CH₃) CH₂=CCH₃, 1H), 2.09 (s, CH₃C=CH₂, 3H). ¹³C NMR (CDCl₃): 149.21 (NCH=C, 1C), 134.84 (NCH₂C, 1C), 133.56 (CH₃C=CH₂, 1C), 129.11 (*o*-Ar, 2C), 128.71 (*p*-Ar, 2C), 128.01 (*m*-Ar, 1C), 119.63 (NCH=C, 1C), 112.51 (CH₃C=CH₂, 1C),

54.07 (NCH₂, 1C), 20.65 (CH₃C=CH₂, 1C). Mass Spec for C₁₂H₁₃N₃ Calculated: 199.11; Found (M+H)⁺: 200.12.

Modified Procedure for Synthesis of α -Methylvinyl triazole Derivatives by an Elimination Strategy and an "One-Pot 'Click' Reaction": Synthesis of Methyl 3-(4-(prop-1-en-2-yl)-1,2,3-triazol-1-yl)propanoate (23) is Depicted

To a 100 mL round bottom flask equipped with a magnetic stir bar and charged with deionized water (7 mL) was added (in the following order) sodium azide (1.77 g, 27.26 mmol), sodium L-ascorbate (0.36 g, 1.81 mmol), and CuSO₄ (0.10 g, 0.63 mmol). After stirring until dissolution, dimethylformamide (7 mL, to make a 1:1 H₂O:DMF mixture) was added followed by methyl 3-bromopropanoate (1.05 g, 6.28 mmol), and 2-methyl-3-butyn-2-ol (0.81 g, 9.65 mmol). The resulting reaction mixture was allowed to stir at 70 °C overnight (16 h). On completion, the reaction mixture was partitioned between CH₂Cl₂ and H₂O and the aqueous layer extracted three times with CH₂Cl₂. The organic fractions were washed once with deionized water, then combined, dried over MgSO₄, filtered and concentrated under reduced pressure. This crude mixture was then purified via flash column chromatography (5:1 ethyl acetate:methanol) to yield 1.25 g (90%) of 3-(4'-(2''-hydroxypropan-2''yl)-1',2',3'-triazol-1'yl)propanoate, **22**, as a clear oil.

¹H NMR (200 MHz, CDCl₃): 7.53 (s, ArH, 1H), 4.62 (t, *J* = 6.5 Hz, NCH₂CH₂, 2H), 3.68 (s, COOCH₃, 3H), 2.95 (t, *J* = 6.5 Hz, NCH₂CH₂, 2H), 2.61 (s, OH, 1H), 1.60 (s, C(CH₃)₂OH, 6H). ¹³C NMR (CDCl₃): 170.91 (COOCH₃, 1C), 155.59 (NCH=C, 1C), 120.31 (NCH=C, 1C), 68.02 (C(CH₃)₂OH, 1C), 51.93 (COOCH₃, 1C), 45.23 (NCH₂, 1C), 34.16 (NCH₂CH₂, 1C), 30.17 (C(CH₃)₂OH, 2C). Mass Spec for C₉H₁₅N₃O₃ Calculated: 213.11; Found (M+Na)⁺: 236.10.

A similar reaction condition described above for **49** was applied for **22** and gave **23** as a clear oil (90% yield).

¹H NMR (200 MHz, CDCl₃): 7.57 (s, ArH, 1H), 5.63 (dd, *J* = 1.5, 0.9 Hz, *cis*(to CH₃) CH₂=CCH₃, 1H), 5.01 (p, *J* = 1.6 Hz, *trans*(to CH₃) CH₂=CCH₃, 1H), 4.58 (t, *J* = 6.4 Hz, NCH₂CH₂, 3H), 3.63 (s, OCH₃, 3H), 2.91 (t, *J* = 6.4 Hz, NCH₂CH₂, 2H), 2.05 (dd, *J* = 1.0, 0.4 Hz, CH₃C=CH₂, 3H). ¹³C NMR (CDCl₃): 171.09 (COOCH₃, 1C), 148.63 (NCH=C, 1C), 133.53

(CH₃C=CH₂, 1C), 120.68 (NCH=C, 1C), 112.45 (CH₃C=CH₂, 1C), 52.17 (OCH₃, 1C), 45.45 (NCH₂, 1C), 34.46 (NCH₂CH₂, 1C), 20.64 (CH₃C=CH₂, 1C). Mass Spec for C₉H₁₃N₃O₂ Calculated: 195.10; Found (M+H)⁺: 196.11.

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